PREDICTION OF HIGH TEMPERATURE GREASE LIFE USING A DECOMPOSITION KINETIC MODEL

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ABSTRACT

A decomposition kinetic model was developed based on thermodynamic theory, first-order reaction law, and PDSC and modified TGA techniques. This kinetic model is able to predict grease degradation life at various temperatures using their activation energy. In addition, the kinetic model was found to have a good correlation with the ASTM D 3527 test method that was simulated using a front wheel bearing system. The advantage of this kinetic model is that it can evaluate the grease thermal-oxidation stability and predict the high temperature grease decomposition life within a short period. It also appears that this kinetic model is potentially useful for grease screening, quality control, and base oil composition effect in thermal-oxidation stability. This paper details how to develop a decomposition kinetic model, its correlation to a bearing test, applications and findings.

INTRODUCTION

Lubricating greases are currently used in various mechanical systems designed for open lubrication system such as automobile wheel bearings, chassis systems, and gearboxes. The high temperature service life of grease is an important operational parameter in these mechanical systems. This property usually defines the upper operational temperature in service. For the last several decades, numerous ball-bearing and roller-bearing grease endurance tests have been devised for laboratory evaluation of grease. Some of them were used to standardize specific test procedures in the grease industry, while others were used in individual laboratories for grease development. Among them, the ASTM D 3527 test method, Life Performance of Automotive Wheel Bearing Grease, is widely used in the grease industry and by users. This test method comprehensively evaluates all individual physical and chemical properties of greases directly related to high temperature and shear, using a simulated front wheel bearing system. The disadvantage of this method is its poor test precision, long endurance testing time, and questionable correlation with the field vehicle under operating conditions[1]. For this reason, it has not been extensively utilized in grease research and development or in the development of specifications. For the last several decades, many researchers had contributed their efforts to develop a modeling system that can predict grease high temperature life. Unfortunately, there is no modeling system available at this time to predict grease life.

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Therefore, a study is needed to define, measure, and develop a modeling system to predict a grease decomposition life.

In a previous study, a kinetic model was developed to predict the grease high temperature life using a Pressure Differential Scanning Calorimeter (PDSC) technique and thermodynamic theory[2]. This PDSC kinetic model tends to determine the oxidation stability of lubricants and their thermodynamic properties. This kinetic model is able to predict induction times and reaction rate constants at various temperatures. Because of its lack of thermal stability measurement capability, the PDSC kinetic model has a limited correlation to the ASTM D3527 test. Especially, this kinetic model has a limitation on grease having excessive oil separation or poor thermal stability. The excessive oil separation can create the insufficient amount of grease in a bearing and leads a shorter high temperature life. In high temperature grease applications, the thermal stability of grease tends to contribute to the quantity of grease, while the oxidation stability can control the quality of grease. Generally, the degradation of greases result from excessive bleeding or evaporation of base oil and oxidation reactions, which increase as temperature is raised. Both properties can affect simultaneously the service life of grease in bearing applications.

Thermogravimetric Analyzer (TGA) is a thermal analysis technique and has been used to measure lubricants thermal stability and to reveal weigh loss decomposition profiles[3]. Although this technique was not originally designed to measure the oil separation of greases under high temperatures, it has potentially a capability to evaluate the grease thermal stability with a minor modification of sample pan. To further develop the decomposition kinetic model, a study was conducted using thermodynamic theory, a modified TGA technique and PDSC kinetic model. This decomposition kinetic model has resolved the previous problems mentioned above and a capability to predict the grease high temperature life within a short time, and provides a good correlation to the results from ASTM D 3527 grease life tests.

DECOMPOSITION KINETIC MODEL

The grease high temperature life is usually associated with its thermal and oxidation stability among many other properties. The deterioration of greases generally results from excessive bleeding or evaporation of base oil and oxidation reactions[4]. The thermal stability of grease tends to contribute to the quantity of grease, while the oxidation stability can control the quality of grease in its high temperature service life. Both properties can affect simultaneously to the service life of grease. In a previous study, a PDSC kinetic model was developed based on the oxidation stability of greases. But, it was found that the PDSC kinetic model limits the prediction capability of grease life due to the absence of thermal stability. Currently, many standard test methods are available to determine the thermal stability of greases, but none of them provides comprehensive data related to the oil separation and evaporation of greases within a short time.

Thermogravimetric Analyzer (TGA) is a thermal analysis technique which measures the amount and rate of change in the weight of a material as a function of temperature and time in controlled atmosphere. For the study, a TGA pan was modified to make pinholes on the bottom of pan in order to measure oil separation during the test. This pinhole pan was made using a sawing needle (diameter: 0.6 mm) and was designed to measure simultaneously both oil separation and evaporation loss of greases. Figure 1 shows a schematic diagram for a modified TGA system. The pinhole pan is shown in Figure 2 with a standard TGA pan.

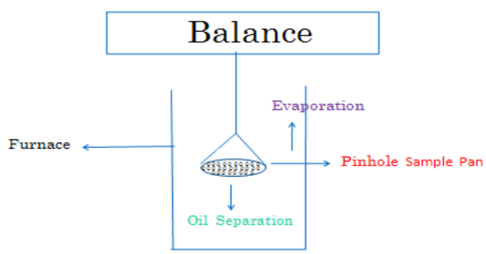

Fig 1. Schematic Diagram for TGA with Pinhole Pan

Fig 2. Photos for Pinhole pan and Standard TGA pan

To verify this modified TGA system, the Grease A was tested at 180 °C for two hours using both pans. The test results are shown in Figure 3 and clearly indicated that the pinhole pan allows the oil separation of grease compared to the result of the standard TGA pan.

This procedure is a very similar to the ASTM D6184 grease cone bleeding test except for the automatic data collection.

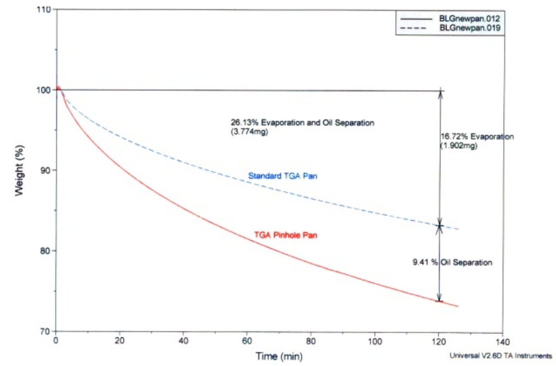

Fig 3. TGA profiles using Standard and Pinhole pan

To develop a decomposition kinetic model, ten grease samples were selected and tested according to the ASTM E 1131 TGA test method with a pinhole pan under nitrogen environment. Table 1 provides grease identification and their physical properties. Most greases are currently used in the rolling element bearing applications. In searching for a rate equation, TGA data obtained from Grease A was plotted on Figure 4 in a first- order kinetic equation format which is independent of the initial concentration of sample. The resulting graph shows the data points fall on straight lines through the origin which met the criteria of first-order equation. This first-order kinetic equation may be expressed in terms of fractional conversion x and the rate constant k which depends on the temperatures[5]. Assume that no oxidation is involved in this equation.

$$t = -\frac{\ln(1-X)}{k} \qquad [1]$$

where

t: grease decomposition life, hr

x: weight loss

k: reaction rate constant, min^{-1}

Table 1. Grease Identification and Physical Properties

Code	Grease	Base oil Type	Thickener	NLGI Consistency Number	Dropping Point, °C	Evaporation Loss @ 180 °C, %	PDSC @ 180 °C, min
A	Automotive Grease	PAO +Mineral	Li-complex	2	256	6.5	35.8
B	Aviation Grease	PAO	Clay	2	343	3.5	>120
C	Airframe Grease	Ester	Clay	2	282	6.4	>120
D	Helicopter Grease	Mineral	Calcium	2	151	41.2	5.4
E	Moly Grease	Ester	Clay	3	263	5.2	>120
F	Instrument Bearing Grease	Ester	Lithium	2	187	11.7	112.8
G	NLGI EP, Batch 6	Mineral	Lithium	2	200	17.3	74.3
H	Biodegradable Grease	Polyol Ester + PAO	Li-complex	2	306	7.7	87.1
I	NLGI Reference Grease Batch 10	Mineral	Lithium	1	194	19.2	44.7
J	Aviation Grease	Ester	Clay	1	321	2.4	>120

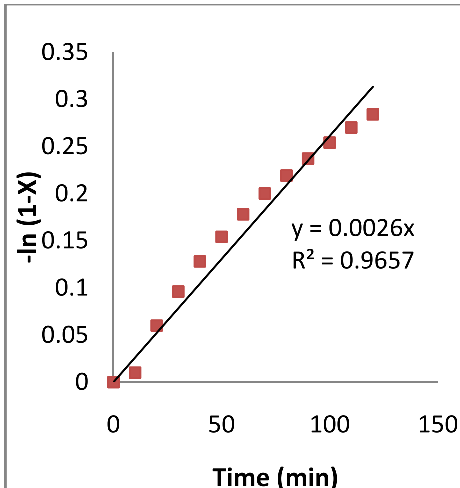

Fig 4. First Order Reaction of Grease A

The rate constant (k) of first-order kinetics is directly calculated from TGA decomposition data[6]. Let a be set as 100 % at t = 0 and b is the percentage weight loss at any other time denoted by t_1 (i.e., 120 minutes). The reaction rate for weight loss is: db/dt = k (a-b). On integration, this equation becomes:

$$k = \frac{1}{t1} \ln \left(\frac{a}{a-b}\right) \qquad [2]$$

where

a= 100 %
b : percentage of concentration loss at 120 minutes
t_1 = 120 minutes

This rate constant (k) is also associated with the Arrhenius' Law, which is based on a theoretical relationship between chemical reaction rates and temperatures[7]. The Arrhenius model has

a reciprocal scale for absolute temperature and a natural logarithmic scale for k. This Arrhenius plotting technique is often used to determine whether the reaction can be fitted into Arrhenius' Law and the first-order rate equation which gives a reasonably straight line on the plotting and the slope of this equation is proportional to the activation energy. Generally, the activation energy (E) of each grease at given reaction is considered as constant and independent from temperatures[5]. The reaction with high activation energies is much more temperature-sensitive than those of low activation energies.

$$k = ko\, e^{-\frac{E}{RT}} \qquad [3]$$

k_o is a frequency factor and R is a universal constant (8.314 J/mol. K). E is denoted as activation energy. In this equation, raising the temperature increases the reaction rate (k). This kinetic equation represents the negative straight line with respect to 1/T and its differential equation is as follow:

$$\frac{d \ln k}{d\left(\frac{1}{T}\right)} = -\frac{E}{R} \qquad [4]$$

E/R represents a slope of the Arrhenius equation and can be determined based on the experimental data. To verify this reaction, Grease A and B were tested at three different temperatures (i.e., 160, 180, 200 °C) and the test results were reported in Table 2 and plotted in Figure 5 using the Arrhenius polling technique. It clearly demonstrates that the reaction rate constant (k) of both greases follows the Arrhenius' Law that depends on temperatures.

Table 2. Rate constant (k) of Test Grease at Various Temperatures

Temperature (°C)	Grease A (min^{-1})	Grease B (min^{-1})
200	0.0025	0.0022
180	0.00186	0.0013
160	0.001	0.0006

Therefore, the activation energy (E) at given reaction can be also calculated using a TGA two-point calculation method. The following equation requires two reaction rate constants (k_1 and k_2) measured at two different temperatures (T_1, T_2):

$$E = R\,\frac{T1\,T2}{T1-T2}\, ln\left(\frac{k1}{k2}\right) \qquad [5]$$

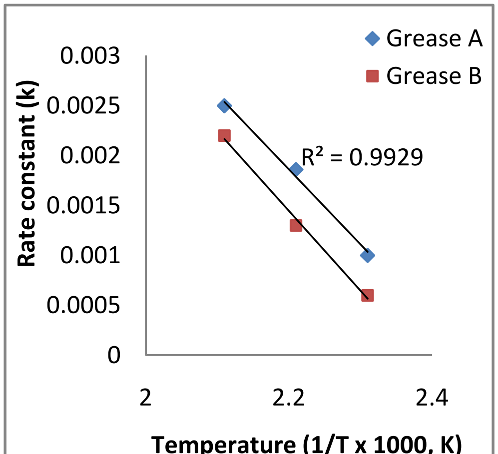

Fig 5. Grease A and B in Arrhenius' Form

Then, the Arrhenius frequency factor (k_o) can be calculated from the following equation. This frequency factor (k_o) is generally a constant at a given reaction and almost independent from temperatures[7].

$$ko = -\frac{\ln(1-Xf)}{t}\, e^{\frac{E}{RT}} \qquad [6]$$

Where

x_f: Final conversion fraction

To develop a grease decomposition kinetic model, Equation 3 is substituted into Equation 1, resulting in Equation 7.

$$t = -\left(\frac{1}{ko}\right)\ln(1-X)\, e^{\frac{E}{RT}} \qquad [7]$$

In the TGA test, the final conversion concentration (X_f) can be assumed to be the same value at each TGA test and denoted as 0.99. Equation 7 can be rewritten in the following form.

$$t = \frac{4.6}{ko} e^{\frac{E}{RT}} \qquad [8]$$

Table 3 demonstrates the thermal stability for Grease A, and shows their thermodynamic properties and its reaction constant (k) at a series of temperatures. The half-life of this reaction is also shown in Table 3. This half-life is often used to differentiate the grease thermal stability.

The grease decomposition life is not only depending on its thermal stability but its oxidation stability. The oxidation stability tends to reduce the grease life obtained from the thermal stability. It was found that the grease decomposition life is reduced exponentially by the coefficient of oxidation, α. In the ASTM D 5483 PDSC procedure, the maximum induction time was designed to be 120 minutes at each test temperature. The coefficient of oxidation (α) can be determined based on the ratio of induction times and was set to range from zero to 1. Therefore, Equation 8 was powered by α and rewritten by Equation 9. This decomposition kinetic model is only a function of temperature and presents in Arrhenius form.

$$t\,(hr) = \left[\frac{\frac{4.6}{ko} e^{\frac{E}{RT}}}{60}\right]^{\alpha} \qquad [9]$$

where

$\alpha = \frac{\text{ti}}{120}$, if $t_i > 120$, then $\alpha = 1$ at test temperature.

t_i : Induction time in PDSC

Table 3. The Predicted Thermal Stability of Grease A

Sample Name	Grease A	
Reaction Rate Constant (k), min^{-1}	0.001	0.00186
Test Temperature	160 ºC	180 ºC
Activation Energy, KJ/mol	50.6	
Slope (E/R)	6086.3	
Frequency factor (k_o)	1272.0	
Temperature, ºC	Rate constant (k), min^{-1}	Half life, min
100	0.00010	66647.9
110	0.00016	4341.7
120	0.00024	2897.7
130	0.00035	1973.2
140	0.00051	1368.8
150	0.00072	966.2
160	0.0010	693.0
170	0.00137	504.6
180	0.00186	372.6
190	0.00249	278.7
200	0.00328	211.1
210	0.00428	161.7

Table 5 lists the decomposition kinetic life of the tested greases and their thermodynamic properties. This kinetic model requires two rate constants obtained at two different temperatures from a modified TGA and induction time from PDSC. In this equation, the oxidation coefficient (α) also varies with temperatures.

Table 5. Decomposition grease life from Kinetic Model

Grease	Rate constant (k1), @160 °C	Rate constant (k2), @180 °C	k_o	Slope (E/R)	Activation Energy (E), KJ/mol	Coefficient. of Oxidation (α)	Decomposition grease kinetic life, hrs, 180 °C
A	0.001	0.00186	411.1	5642.9	46.9	0.885	19.1
B	0.0006	0.0013	24201.5	7583.0	63.0	1	59
C	0.00093	0.0036	1.92×10^{10}	13274.4	110.0	1	21.2
D	0.0061	0.0168	5.63×10^{7}	9935.0	82.6	0.045	0.02
E	0.0009	0.0037	7.25×10^{10}	13864.7	115.3	1	20.7
F	0.0023	0.0116	1.9×10^{13}	15869.4	131.9	0.94	5.9
G	0.0013	0.0025	3519.4	6413.4	53.3	0.62	30.6
H	0.0007	0.00106	8.44	4069.5	33.8	0.726	7.29
I	0.0019	0.003	59.1	4479.6	37.2	0.37	0.25
J	0.00025	0.00071	4.63×10^{6}	10237.1	85.1	1	108

CORRELATION WITH ASTM D 3527 TEST METHOD

The ASTM D 3527 test method is widely used to evaluate the high-temperature grease life under specified conditions. The test method is currently specified in the ASTM D 4950[8] and MIL-PRF-10924H[9] automobile grease specifications. To make a correlation between the actual bearing test and a decomposition grease kinetic model, ten greases selected for this study were tested according to the ASTM D 3527 test method. To increase reliability of data, several life data were generated for each sample and the average life data were reported with grease kinetic life in Table 6. For the study, the kinetic life data were generated at 180 °C instead of 160 °C. The reason is that the test temperature (160 °C) specified in the ASTM D-3527 test is measured from the spindle hole in which the thermocouple is inserted, resulting in a temperature gap of about 20 °C between the chamber and spindle. It appears that the test temperature is closer to the chamber temperature instead of the spindle temperature because the test specimen (wheel bearing hub system) is fully open in the chamber and the heat transfer is facilitated by hot air in the chamber. Therefore, the actual test temperature of ASTM D 3527 test method is assumed to be higher than 160 °C (i.e., 180 °C)[2]. All life data listed in Table 6 except for the predicted grease life were plotted on Figure 6 to determine the relationship between the decomposition grease kinetic model and the ASTM D 3527 grease life.

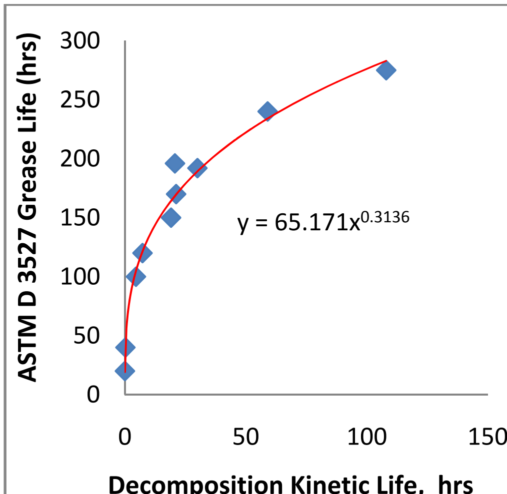

Fig 6, Decomposition Kinetic Life vs. ASTM D 3527 Grease Life

Based on this test result, a high temperature grease life equation was developed using the decomposition kinetic model. Equation 10 presents the grease life in the function of decomposition kinetic life.

$$\text{Grease Life (hrs)} = 65 \text{ x } [t]^{0.32} \quad [10]$$

where

t: Decomposition kinetic life, hr

To verify this equation, all predicted grease life listed in Table 7 was plotted in Figure 7 with the data obtained from the ASTM D 3527 tests. It shows that they have a good agreement. Their correlation coefficient (r^2) was found to be 0.98. In reviewing of data, grease having a long decomposition kinetic life also gave a longer life in the grease endurance test.

Table 6. Grease High Temperature Life and Their kinetic life

Sample	Kinetic Life @ 180 °C, hr	ASTM D 3527, hrs	Predicted Grease Life, hrs
A	19.1	150	167
B	59	240	240
C	21,2	170	174
D	0.02	20	18.6
E	20.7	196	171
F	4.6	100	106
G	30	192	194
H	7.29	120	123
I	0.25	40	41
J	108	275	290

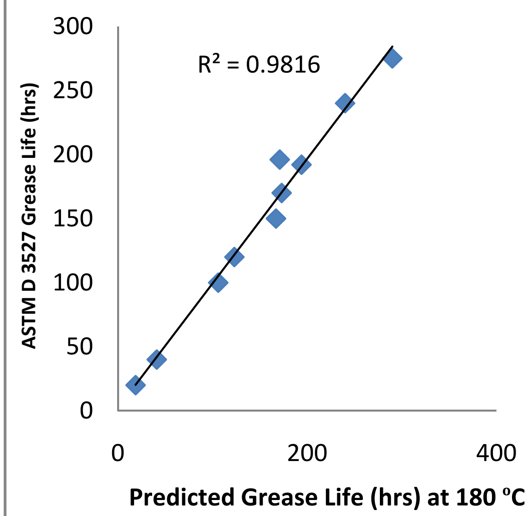

Fig 7. Correlation between actual and predicted grease life

CONCLUSIONS

A decomposition kinetic model for greases was developed based on the thermodynamic theory and a modified TGA kinetics and PDSC kinetic model. This kinetic model can calculate thermodynamic properties and predict decomposition grease life at various temperatures. The advantage of this decomposition kinetic model is that it can predict grease decomposition life using two thermal analyzers (i.e., TGA, PDSC) within a short period.

A correlation equation was also developed between decomposition kinetic model and those obtained from the ASTM D 3527 test. They gave a good correlation and the equation has a capability to predict the ASTM D 3527 grease life using a decomposition kinetic life that is calculated at 180 °C. Their correlation coefficient is 0.98 when compared with actual data. Therefore,

this kinetic model can be effectively used in quality control and the research and development of new products.

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